Bacteria Breakfast

As an environmental threat, worn-out auto and light truck tires might not have the cachet of other, more "glamorous" waste materials such as chemical or nuclear weapons, yet according to data presented at a 1990 hearing of the House Subcommittee on Environment & Labor, there are more than two billion waste tires stockpiled in this country, with another 250 million tires being added each year, and these tires present a variety of threats to human health.

A 1995 report by the Scrap Tire Management Council states that there are approximately 900 million tires located in municipal solid waste landfills. Landfill operators are increasingly reluctant to accept tires because of health concerns—tires make ideal breeding places for rats and mosquitoes and, when burned, can release hazardous materials including soot, benzene, sulfur, and heavy metals. During landfill fires, surface heat can melt tires buried below. Because tires are 25% petroleum products by weight, oil and other petroleum compounds can pass into soil and groundwater. Because of such hazards, according to the Institute of Scrap Recycling Industries (ISRI), about 25 states have already implemented landfill bans on scrap tires or are preparing to do so. Researchers are scrambling to develop innovative ways to dispose of used tires and scientists at Pacific Northwest National Laboratories (PNNL) have uncovered one possible solution.

More Tires than Cars

Kimberley Harris, a market analyst for ISRI, says there is a wide range of markets for used tires in the United States, including the use of whole tires in reef construction, civil engineering projects, and erosion control, and the use of processed tires in brake pads and athletic and recreational surfaces. But Harris adds that, even with all of these potential markets, there are far more tires available than are needed.

"Not every tire is accessible," Harris points out, "nor are all of them recyclable. Dirt is a big problem, as is chemical damage and damage from UV rays. It probably wouldn't be unreasonable to approximate, given all the different circumstances of the industry, that we currently recycle less than 10% of the total."

It would seem that the most elegant, environmentally friendly solution would be to "close the loop" by turning old tires into new ones. Recyclers can turn old cans and bottles into new ones and old newspapers into today's daily, so why not just remove the landfill problem and ease the environmental impact of rubber production by turning yesterday's blowout into tomorrow's new whitewall?

In 1993, the total volume of ground tire rubber (GTR) used represented the recycling of less than 13% of the total number of tires added to the waste stream that year; clearly, the problem is too complex to respond to any single solution. "Tire recycling," says PNNL chemist Robert Romine, "is a market with tremendous potential [with] perhaps 600 million pounds [available] annually, but there are a few serious problems recyclers haven't been able to address satisfactorily. It's not just a matter of grinding up old tires and turning them into new ones. It would be nice if it were that simple, but it's not." The reason lies in the process that creates a tire from virgin rubber, says Romine. Rubbers, both natural and synthetic, are referred to as elastomers, and in their raw, unmodified form, are not only weak and adhesive, but lose elasticity with use, have physical properties that change markedly with temperature, and are degraded by air and sunlight.

"The nature of the carbon-based rubber molecule is such that, without any alteration, it creates a material with the basic consistency of Silly Putty," Romine says. "Obviously, that wouldn't make for a great tire, so what tire manufacturers settled on was a process called 'vulcanization,' where the virgin rubber is heated and combined with elemental sulfur. That, in turn, leads to the formation of a series of crosslinks, which stiffens the material [and makes] it more elastic, so it can stretch under stress, and then recover." Romine continues, "The problem at that point is that the material doesn't have a lot of chemical reactivity left. It's a very stable chemical state, which makes for a good tire, but something that's very difficult to recycle, because if you just grind it up and try to mix it with virgin rubber, there's no way for bonds to be formed."

Since early this century, Romine says, "people have been doing chemical conversion of waste tire material. In fact, until the early 1970s, there was a significant industry using some very harsh processes involving heat and caustics to liquefy waste rubber. That industry no longer exists, due in large part to the economics of dealing with what was a very hazardous waste stream."

Romine continues, "Today, there are people looking at processing rubber with chlorine and sulfur dioxide, substances harsh and dangerous in and of themselves, which still produce hazardous wastes that must be carefully disposed of. The problem is to find a way to break those carbon-sulfur crosslinks without using or creating something dangerous."

Breaking It Down

In science, solutions to significant problems sometimes occur under the unlikeliest of circumstances. Newton may or may not have conceived the laws of gravity by watching an apple plummet to earth, but Romine and his wife Margaret, a microbiologist at PNNL, happened on their discovery over a bottle of red wine. "It was one of those chance cross-fertilizations of fields," Romine says. "We were just talking about microorganisms and the things they can do, many of which we're just beginning to learn about, and *Sulfolobus* came up."

Sulfolobus acidocaldarius grows at a pH level of 2.5 at temperatures of 70°C, and thrives in, among other places, the inhospitable hot springs of Yellowstone National Park. What makes *Sulfolobus* so special to Romine is the bacteria's food of choice—sulfur.

Initially, Romine studied five different bacteria for their effect on GTR: *Thiobacillus ferooxidans, Thiobacillus thiooxidans, Rhodocossus rhodochrous-IGTS8, Sulfolobus acidocaldarius,* and an unidentified bacterium from the American Type Culture Collection. Romine conducted a seven-day experiment, during which the bacteria were fed GTR and ion chromatography was used to monitor the biodesulfurization of the GTR. By analyzing the concentration of sulfate in solution, it was possible to determine which of the microorganisms were most effective at breaking down the GTR. The results showed that *Sulfolobus* was far and away the most effective, converting 13.4% of the sulfur within the seven-day period. The next most effective was a mix of *T. ferooxidans* and *T. thiooxidans,* at 10.5%.

"We discovered that when you mix *Sulfolobus* with finely ground [74 micron] tire rubber, the bacteria progressively oxidize the crosslinks, thus leaching sulfur off the surface of the rubber molecule," Romine says. "You can't let the reaction run to completion, because then you'll be left with a material that is as nonreactive as unprocessed rubber, but it's actually a fairly simple matter to stop the reaction at any point by either raising the pH or lowering the temperature."

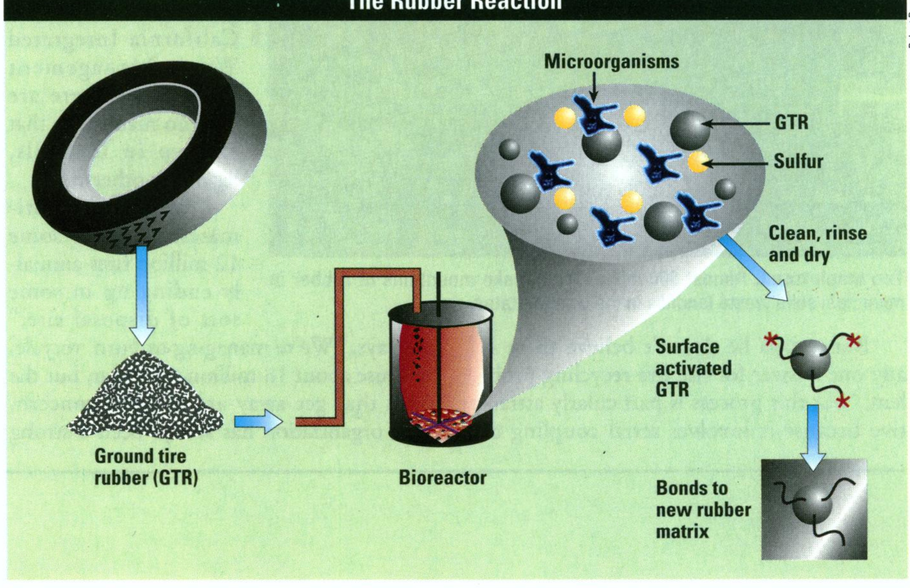
Roughly 48 hours after the reaction begins, what's left, according to Romine, is a substance that can be mixed with virgin rubber in a ratio of about 15% biodesulfurized rubber to 85% virgin rubber, and turned back into a usable material for tires, with no loss in desirable performance characteristics. The only by-product is a mixture of water and dormant microorganisms, which are killed when the cell walls lyse during the waste-water treatment process. "That's one of the beauties of this process," says Romine, "It produces absolutely nothing that's environmentally harmful, which means that, not only is it much safer, it is also far more economical than traditional methods, which used toxic chemicals and produced a whole series of harmful by-products that had to be handled very carefully."

Romine has dubbed *Sulfolobus* a "smart" bacteria because it treats the carbon-based rubber molecule as an unsuitable substrate on which to grow, targeting instead the crosslinked sulfur. "Think of the rubber molecules as a plate of spaghetti without sauce," Romine suggests. "If you tilt the plate, the noodles slip and slide past one another, but if you put on a thick sauce, things bond together. That's vulcanization. What *Sulfolobus* does, in effect, is ignore the noodles and eat up the sauce, thus freeing the noodles to mix with more noodles and be ready for additional sauce."

The tire industry is the biggest and most obvious target for products of this technology, Romine says, but the market for this biodesulfurization process extends to encompass a tremendous range of rubber products, including hoses, belts, conveyor belts, and other items currently viewed as automatic landfill material.

"In this country," says Romine, "the driving forces behind auto recycling are the 'Big Three' [auto manufacturers] and the big tire manufacturers, who have told their

The Rubber Reaction



Robert Romine

suppliers, 'You have to give us a 10% recycled-content tire.' Because of the safety factor, and the high heat and wear stresses tires must deal with, the standards of the industry are naturally very high, but we are confident we can meet them. We're smoothing out the process on a smaller scale. Then the challenge will be to scale up from the lab to a real commercial process."

For the past two years, Romine has been working with Rouse Rubber Industries, Inc., a Vicksburg, Mississippi, tire grinding facility, to build a pilot project to demonstrate his biodesulfurization process. "Tire grinding plants are ideal to work with," he says, "because their whole process generates a lot of excess energy in the form of heat, heat we can use to run our bioreactor, thus further reducing the cost of the process."

Romine built a 200 liter bioreactor, using the same type of process and control equipment that would be used in a pilot or full-scale facility, and successfully produced 70 pounds of surface-treated GTR. Operating under what he calls a "handshake agreement" with Mike Rouse of Rouse Rubber, Romine then built a 2,000 liter fermentation reactor capable of producing enough rubber for 3,000 tires a month. "We're still working out some of the mechanical bugs on that system, no pun intended," he says. "I should think we'll be conducting actual runs of that system this year, and if all goes as I believe it will, we could see actual commercial licensing in the very near future."

International Tire & Rubber Association

Too much tread. Almost 900 million tires make mountains of rubber in municipal solid waste landfills in the United States.

Rouse says he doesn't believe there is any one answer for the tire recycling problem, "but this process is particularly attractive because it involves serial coupling of our technologies. We produce a very clean, uniform, high-surface-area rubber product, and [Romine's] technology lends itself to our type of technology."

Rouse continued, "On paper, the economics of this process look very favorable. It's a wet technology, like ours, and it doesn't produce a toxic waste stream, like the older methods of tire recycling. We've looked at many different surface treatment methods, most of which are very capital-intensive, but [this one] isn't. [It's] just taking microorganisms that have been on Earth for millions of years and letting them do what they do naturally. It doesn't hurt the rubber, there are no environmental concerns, and it fits nicely into our system. To this point, it looks like a winner."

Tires, Tires Everywhere

With more cars than any other state, California is struggling to deal with a flood of more than 29 million used tires generated annually. The state has set up a fund to provide more than $2 million in grants and loans for tire recycling projects, but Martha Gildart, manager of the secondary material and technology branch of the California Integrated Waste Management Board, says there are still too many tires that end up in landfills, legally or otherwise.

"By our best estimates, there are some 12 million tires annually ending up in some sort of disposal site," she says. "We're managing to burn, recycle, or reuse about 18 million each year, but the ones that get away are of great concern. Our organization has always been a strong proponent of closed-loop recycling—turning something back into whatever it was before, and . . . [this process] sounds promising. I would have some concerns about the concentration of sulfur being flushed away in the waste stream, although most sewer systems are designed to handle fairly high levels, and I think when you're using that fine a grind, you start getting into questions of energy consumption versus overall return, but in general, it sounds like a promising technology."

"This process isn't a silver bullet, not by any means," Romine admits. "But I could see it increasing the number of tires recycled in this country by 20 percent. I can also see this process working for other rubber-containing products like belts and hoses, thus pulling more of them out of the waste stream."

What's so exciting about this technology, according to Romine, is that it involves taking a closer look at the microorganisms around us, how they live, and what they can do. Says Romine, "It's like finding cures for cancer in rainforest plants; we have no idea what's out there until we begin to take a close-up, serious look."

Although Romine believes this and other technologies will change used tires from a waste material to a commodity, it will not solve the whole problem. Says Romine, "There are some states, such as Illinois, that are actually net importers of waste tires because they've found ways to deal with their waste tire population and have expanded their market, but it's only when we see [recycling] on a national basis that we can call the waste-tire problem solved. This is just one of the technologies that will lead us to that point."

Lance Frazer

Suggested Reading

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